THE REACTION BETWEEN SULFUR DIOXIDE AND OLEFINS

BY

WILLIAM HENRY SHARKEY

B.S., Oklahoma A. and M. College, 1937

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE SCHOOL OF THE UNIVERSITY
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INTRODUCTION

The steadily increasing volume of work published on the subject of high-molecular-weight compounds has prompted a thorough investigation of products obtained by the interaction of sulfur dioxide and olefins. The structure of these polysulfones has been established[1,2] as the "head to head, tail to tail" type. The present study was undertaken to extend the knowledge of the chemical properties of these polymers with especial emphasis on a method of preparation and purification which would lead to more stable polysulfones.

DISCUSSION AND EXPERIMENTAL

It has been known for some time that organic peroxides,[3] nitrates, and silver salts[4] promote the interaction of sulfur dioxide and olefins to give polysulfones. Urea peroxide is an effective catalyst for this reaction and ultraviolet light will promote the formation of polysulfones from α-olefins and sulfur dioxide.

Trimethylamine oxide, triamylamine oxide, and dimethylaniline oxide catalyze the interaction of sulfur dioxide and olefins. These amine oxides demonstrate greater catalytic effect if they are used in conjunction with halogen acid, which suggests that the catalytic action is dependent upon the formation of the hydroxytrialkylammonium ion, an ion soluble in the reaction mixture. The fact that tetramethylammonium chloride and tetraethylammonium bromide catalyze the reaction supports this hypothesis. Other nitrogen compounds, such as hydroxylamine hydrochloride and phthalimide, exhibit slight catalytic action, but hydrazine hydrate, phenylhydrazine, 3,5-dinitrophenylhydrazine, cupferron, phenylglyoxal oxime, semicarbazide hydrochloride, hydrazodicarbamide, azoxybenzene, nitrobenzene, 1-pentenepolysulfone, methyl borate, and dimethyl formamide are ineffective.

The reaction between sulfur dioxide and olefins is reversible, as shown by the decomposition that polysulfones undergo when they are heated. The decomposition is not complete at 140°, as the weight lost rarely exceeds 25% when the polymer is heated two hours at this temperature. A comparison of the factors affecting stability of the polysulfones was made, using the per

cent weight lost when heated two hours at 140° as the standard.

Pure polysulfones do not decompose as much under test conditions as crude products. Purification is carried out by reprecipitation; the polymer is dissolved in acetone and then alcohol is added to the solution to reprecipitate the polysulfone. When purified by several of these reprecipitations, 1-pentenepolysulfone loses 1-2% of its weight under test conditions. Probably, the function of the purification process is to remove peroxide originally present as a catalyst, as peroxides increase the per cent weight lost under test conditions. However, incorporation of hydroquinone in the polysulfone does not improve the stability to heat at 140°.

Polysulfones prepared from olefins containing a trace of allyl bromide are more stable to heat than those prepared from pure olefins. 1-Butenepolysulfone, 2-butenepolysulfone, 1-pentenepolysulfone, 1-hexenepolysulfone, and 1-heptenepolysulfone prepared from olefins containing a trace of allyl bromide lost less than 1% of their weight under test conditions. *p*-Bromobenzyl chloride produces a similar effect, but allyl chloride, allyl alcohol, ethyl bromide, crotyl bromide, benzyl bromide, *β*-bromostyrene, undecylenyl bromide, 1-bromoheptene, *p*-bromo-2-methylallyl benzene, chloromethylmesitylene, chloromethyl ether, chloroform, carbon tetrachloride, benzyl alcohol, furyl alcohol, furylacrylic acid, ethyl acrylate, camphene, and heptyl mercaptan do not.

By heating a dioxane solution of a polysulfone containing about 20% of allyl bromide, crotyl bromide, 1-bromoheptene, or ethyl acrylate under reflux for five hours, a polymer that loses less than 1% of its weight under test conditions is produced, even though the original polysulfone may have decomposed to a greater extent. This is a modification of a process described by Wilder.[5] The use of camphene or cyclohexene in a similar fashion has no effect upon the heat stability of the polysulfone.

The per cent weight lost by a polysulfone is greatest for the first two hours of heating; prolongation of the heating period for an additional two hours does not cause as much further decomposition. The per cent weight lost for propylenepolysulfone, 1-pentenepolysulfone and 1-hexenepolysulfone during the second two hours of heating is of the order of 0.05-0.10%.

The per cent weight lost by a polysulfone under test conditions at 140° decreases with the age of the polymer. In this, as in the

other cases discussed, the chemical changes that take place rendering the product more stable to heat are not known.

The molecular weight of a polymer has no apparent relation to its heat stability. Also, the presence of acids neither harms nor improves the stability to heat of these products.

BIBLIOGRAPHY

[1] Hunt and Marvel, J. Am. Chem. Soc., **57**, 1691 (1935).

[2] Glavis, Ryden, and Marvel, *ibid.*, **59**, 707 (1937).

[3] Frederick, Cogan, and Marvel, *ibid.*, **56**, 1815 (1934).

[4] Snow and Frey, Ind. Eng. Chem., **30**, 176 (1938).

[5] Wilder, U. S. Patent 2,146,276 (1939).

VITA

The writer was born in Vinita, Oklahoma, on October 7, 1916. He received elementary training at St. Mary's Academy in Ponca City, Oklahoma, and in Ponca City High School, from which he was graduated in 1933. In September of 1933 he entered Oklahoma A. and M. College and was graduated with the degree of B. S. in Chemical Engineering in 1937. From September, 1937, to the present time he has been a teaching assistant in chemistry at the University of Illinois.